(54) Title: A STAMP HAVING AN ANTISTICKING LAYER AND A METHOD OF FORMING OF REPAIRING SUCH A STAMP

(57) Abstract: A stamp for use in transferring a pattern in nano-scale has a monomolecular antisticking layer. The anti-sticking layer comprises molecular chains, which are covalently bound to the surface of the stamp and which each comprise at least one fluorine-containing group. Each molecular chain contains a group Q, which comprises a bond which is weaker than the other bonds in the molecular chain as well as the covalent bond that binds the molecular chain to the surface of the stamp. Splitting of said bond in the group Q creates a group Q1, which is attached to the part of the molecular chain being left on the surface of the stamp and which is capable of reacting with a fluorine-containing compound to restore the antisticking layer. In a method of manufacturing a stamp for use in transferring a pattern in nanoscale, the stamp is provided with the above-mentioned molecular chain. In a method of repairing a damaged antisticking layer of the above-mentioned stamp, the stamp is treated with a repairing reagent, which has a coupling end, which is capable of reacting with the group Q1, and a fluorine-containing group located at the other end of the repairing reagent.

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A STAMP HAVING AN ANTISTICKING LAYER AND A METHOD OF FORMING AND A METHOD OF REPAIRING SUCH A STAMP

Field of the Invention

The present invention relates to a stamp for use in transferring a pattern in nanoscale, which stamp has a monomolecular antisticking layer.

5   The invention also relates to a method of manufacturing a stamp for use in transferring a pattern in nanoscale, which stamp has a monomolecular antisticking layer.

The invention further relates to a method of repairing said monomolecular antisticking layer.

10   ### Background Art

In the replication of nanostructures, use is often made of a stamp, which hot embosses a pattern into a plate coated with a suitable polymer, such as a thermoplastic. It is necessary to provide an antisticking

15   boundary surface between the patterned stamp and the polymer to prevent thermoplastic from getting stuck to and contaminating the surface of the stamp when the stamp is released from the coated plate after embossing. Also the pattern replicated on the plate can be damaged by

20   such sticking. For successful embossing, the stamp must thus be chemically and mechanically stable and have a low tendency to stick to polymers.

In Microelectronic Engineering 35 (1997) 381-384, R.W. Jaszewski et al. disclose that the surface of the

25   stamp can be covered with an ultra-thin, antisticking layer of PTFE. The layer is precipitated by means of plasma polymerisation or ion sputtering from a plasma. According to Jaszewski et al., the quality of the film deteriorates in the embossing. Obviously, the film is not

30   sufficiently stable.

Summary of the Invention

According to the present invention, the above drawbacks are obviated or reduced and a stamp with an anti-

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sticking layer is obtained, which is stable, has good
antisticking properties and can easily be repaired when
damaged or worn.

        More specifically, the invention provides a stamp
5   for use in transferring a pattern in nanoscale, which
    stamp has a monomolecular antisticking layer and is
    characterised in that said antisticking layer comprises
    molecular chains, which are covalently bound to the
    surface of the stamp and which each comprise at least
10   one fluorine-containing group, each molecular chain
    containing a group Q, which comprises a bond which is
    weaker than the other bonds in the molecular chain as
    well as the covalent bond that binds the molecular chain
    to the surface of the stamp, splitting of said bond in
15   the group Q creating a group Q1, which is attached to the
    part of the molecular chain being left on the surface of
    the stamp and which is capable of reacting with a
    fluorine-containing compound to restore the antisticking
    layer.

20   The invention further relates to a method of manu-
    facturing a stamp for use in transferring a pattern in
    nanoscale, which stamp has a monomolecular antisticking
    layer, said method being characterised in that the sur-
    face of the stamp is provided with molecular chains,
25   which are covalently bound to the surface of the stamp
    and which each comprise at least one fluorine-containing
    group and a group Q, which comprises a bond which is
    weaker than the other bonds in the molecular chain as
    well as the covalent bond that binds the molecular chain
30   to the surface of the stamp, splitting of said bond in
    the group Q creating a group Q1, which is attached to the
    part of the molecular chain being left on the surface of
    the stamp and which is capable of reacting with a
    fluorine-containing compound to restore the antisticking
35   layer.

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The invention also relates to a method of repairing a damaged monomolecular antisticking layer on a stamp as stated above, which method is characterised in

that the stamp is treated with a repairing reagent,
5   which has a coupling end, which is capable of reacting with the group Q1, and a fluorine-containing group located at the other end of the repairing reagent,

that the coupling end of the repairing reagent is bound to the group Q1 which is attached to the surface
10   of the stamp, the group Q being formed anew.

Further advantages and features of the invention will be apparent from the description below and the appended claims.

Detailed Description of the Invention

15   A non-limiting example of transferring a pattern in nanoscale is nanoembossing lithography or nanoimprint lithography, which is a technique for mass-production of nanostructures. A stamp is provided with a nanopattern on its surface. The stamp is heated and pressed against a
20   substrate which is coated with a polymer layer, whereby the pattern is transferred to the polymer layer. Nano-imprinting is described in more detail in US 5,772,905 and US 5,259,926. The stamp according to the present invention can also be used in other embossing processes.

25   The expression "nanoscale" is not to be understood as only relating to structures within the range of sub-micrometers, that is, structures having a size within the range of 1-1000 nm. A stamp often has a pattern with structures within the range of submicrometers as well as
30   structures with a size of up to 100 micrometers and more, for instance up to about 5 mm. The present invention is preferably applicable to stamps comprising structures within the range of submicrometers and/or within the range of 1-100 micrometers. The best effect of the inven-
35   tion is achieved with structures within the range of submicrometers since such structures are relatively more sensitive to sticking when releasing the stamp.

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The present invention is based on the discovery that
a stable antisticking layer can be provided on the sur-
face of the stamp by attaching molecular chains to the
stamp which have antisticking properties. The molecular
5   chains are formed in such a manner that the antisticking
properties can easily be recreated when the antisticking
layer is worn after being used for some time.

The surface of the stamp is conveniently made of a
material M which is suitable for producing nanostructured
10   patterns. Examples of such materials M are Si, Al, Ti,
Ni, Cr and oxides thereof. Si is particularly suitable
since it has satisfactory hardness and is easy to work
when forming patterns in nanoscale. If the surface is
made of metal, such as Al, Ti, Cr, Ni, it is normally
15   preferable for the surface to have an oxide layer. To
obtain a stronger oxide layer, the surface can be oxi-
dised, for instance by means of an oxygen plasma. In some
metals, such as Ni, Cr, it is particularly suitable to
generate such a stronger oxide layer.

20   According to a preferred embodiment of the inven-
tion, a first and a second reagent are used. The first
reagent is bound in a first reaction to the surface of
the stamp, whereas the second reagent is bound in a
second reaction to the first reagent. The reason why this
25   embodiment is preferred is that it is relatively easy to
obtain commercially available compounds which can suit-
ably be used as first and second reagents.

A first reagent to be used in manufacturing the
stamp according to the invention has at least two func-
30   tional groups. A first functional group is intended to
bind to the surface of the stamp. One example of such a
first functional group is a silane group with the formula
$(BO)_{3-n}R'_nSi-$. The silane group can be bound to the sur-
face of the stamp by means of a group B1 on the surface
35   of the stamp, which can be M- or M-O-, where O is oxygen.
In the present application, "silane group" also relates
to the above group after this group has been bound to the

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stamp. The silane group can comprise n aliphatic groups
R' and 3-n reactive binding groups B0, where n=0, 1 or 2.
B0 is suitably a hydrolysable group. Suitable reactive
binding groups B0 are chlorine (Cl) or alkoxy groups,
5   preferably C_{1-4} alkoxy groups, more preferably C_{1-2} alkoxy
groups, such as ethoxy groups (EtO), methoxy groups
(MeO). The aliphatic groups R' are suitably, if they are
at all present, short saturated aliphatic groups, prefer-
ably C_{1-4} alkyl groups, more preferably C_{1-2} alkyl groups
10 such as ethyl groups and methyl groups. When n=1 or 2 and
R' is a methyl group, a smaller binding surface is ob-
tained, that is, the monomolecular layer can be packed
tighter. The strongest bond to the surface is, however,
obtained when n=0, that is, when the silane group has
15 three reactive binding groups B0. Thus, one example of
a suitable first functional group is:

EtO
EtO   - Si-   [first functional group in the
20 EtO   form of triethoxysilane]
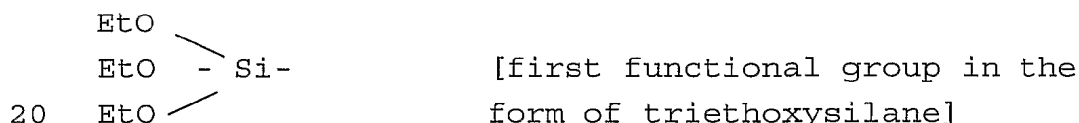
The second functional group X1 of the first reagent
is suitably selected so as not to react or so as to react
only to a limited extent with the surface of the stamp.
25 Such a functional group has the advantage that a homo-
geneous monomolecular layer with a well-defined end group
is provided when treating the surface of the stamp with
the first reagent. Thus, the group X1 is suitably a non-
hydrolysable group. The group X1 should not either react
30 with the first functional group. Suitable groups X1 are,
for instance, -SH, -NH$_2$ and -OH. When X1 is an -NH$_2$ group,
B0 must not be chlorine, since this would result in un-
desirable polymerisation reactions.
The first and second functional groups of the first
35 reagent are suitably attached at two opposed ends of a
carbon compound R1. Preferably, such a carbon compound R1
is a carbon chain, which is unbranched or has short

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branches which suitably have a length of 1-6 carbon
atoms, more preferably 1-3 carbon atoms. The carbon chain
is suitably a saturated, aliphatic carbon chain. Unsatu-
rated carbon chains can participate in undesirable side
5   reactions and highly branched or cyclic compounds take up
unnecessary room at the surface of the stamp, which re-
duces the density of the antisticking functionality on
this surface.

The second functional group X1 can affect the elec-
10   tron density in the closest atoms in the molecule, which
may result in undesirable effects on the first functional
group. Therefore, it is suitable that the R1 group should
have a structure that "isolates", in terms of electron
density, the group X1 from the first functional group.
15   In aliphatic, saturated carbon chains, the CH_2 group
which is situated closest to X1 is highly affected, the
next CH_2 group is somewhat affected, whereas the third CH_2
group is substantially unaffected by X1. The group R1 is
suitably unsubstituted so as not to affect negatively the
20   first and second functional groups. Very long carbon
chains increase the risk of a break on the chain and make
the antisticking layer less stable, as the carbon chains
can change their angle to the surface. Thus, R1 suitably
has a length, from the first to the second functional
25   group, of 1-10 carbon atoms, preferably 2-5 carbon atoms
and most preferably 3 carbon atoms. The group R1 can also
be provided with shorter branches, suitably of a length
of 1-4 carbon atoms, preferably 1-2 carbon atoms, for
instance, with a view to increasing the antisticking
30   functionality or to enhancing the bond to the surface:

$(B1)_3Si-CH_2$
                    $\diagdown$
                         $CH-CH_2-X1$ [branched R1 group with
                    $\diagup$ stronger attachment]
$(B1)_3Si-CH_2$

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$$(B1)_3Si-CH_2-CH \begin{matrix} CH_2-X1 \\ \\ CH_2-X1 \end{matrix}$$

[branched R1 group with more X1 groups]
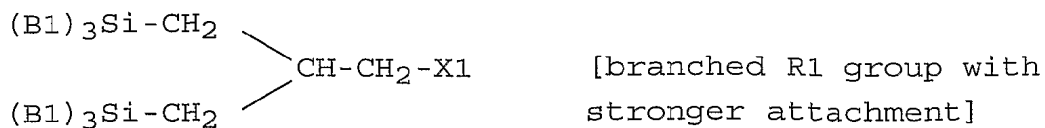
When in the last-mentioned example X1 is -SH, a sulphur bridge S-S usually forms. The sulphur bridge will react in the same way as two separate -SH groups and is therefore equivalent to these groups.
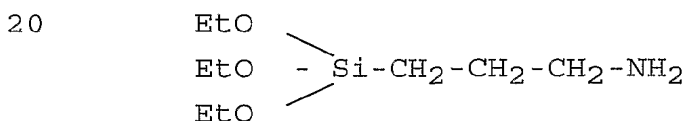
It is suitable to select a first reagent which fulfils the criteria described above and which is available on the market. Examples of preferred first reagents are thus mercaptopropyltriethoxysilane:

$$\begin{matrix} EtO \\ EtO \\ EtO \end{matrix} - Si-CH_2-CH_2-CH_2-SH$$
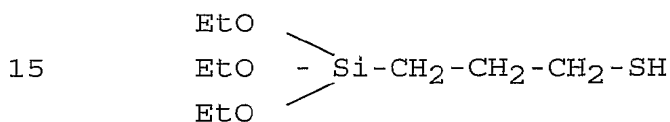
and aminopropyltriethoxysilane:

$$\begin{matrix} EtO \\ EtO \\ EtO \end{matrix} - Si-CH_2-CH_2-CH_2-NH_2$$

The second reagent comprises a first part X2, which is intended to be bound to the X1 group of the first reagent, and a second part R2, which has an antisticking functionality.

The group X2 is selected so as to be suitable for reaction with the X1 group in the first reagent. The reaction should result in a bond which is sufficiently strong to maintain the antisticking functionality at the surface of the stamp. The bond which forms between X1 and X2 is, however, weaker than the other bonds in the mono-molecular layer. Any break on the molecular chain will thus occur in a predictable position, namely between X1 and X2. Examples of suitable combinations of X1 and X2 are: X1 = -SH group and X2 = -SH group, which can form a
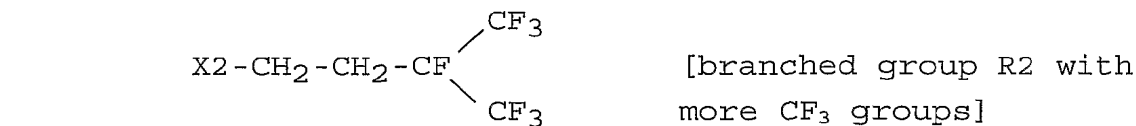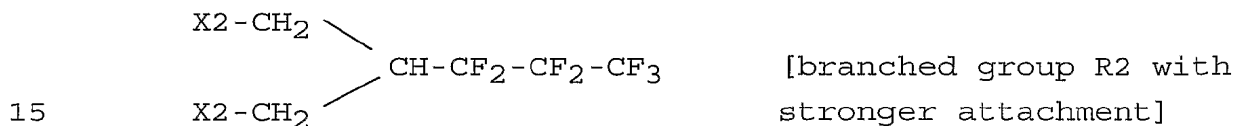
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sulphur bridge, X1 = -NH$_2$ group and X2 = Cl-(C=O)-, which
can form a peptide bond, and X1 = -OH and X2 = HO-(C=O)-,
which can form an ester. It is particularly preferable
that X1 as well as X2 should be -SH groups, since they
5   form a bond which is strong enough to maintain the anti-
sticking functionality, but is weaker than, for instance,
bonds between carbon atoms in the molecular chain,
between carbon atoms and sulphur atoms and between a
silane group and the surface of the stamp.
10   The group R2 suitably contains fluorine atoms, which
yield the desirable antisticking functionality. It is
particularly suitable that R2 should have a free end
group, which contains a carbon atom to which one or more
fluorine atoms are bound. Preferably the group R2 is a
15   fluorinated, aliphatic, saturated carbon chain. Unsatu-
rated carbon chains can participate in undesirable side
reactions and highly branched or cyclic compounds take up
too much space, which reduces the density of the anti-
sticking functionality.
20   The fluorine atoms will affect the electron density
in the closest atoms in the molecule, which may result
in undesirable effects on the bond between X2 and X1.
Therefore, it is suitable that the group R2 should have
a structure that "isolates", in terms of electron den-
25   sity, the X2 group from the fluorine atoms. In aliphatic,
saturated carbon chains, the CH$_2$ group closest to a car-
bon atom, which is substituted with fluorine, is highly
affected, whereas the next CH$_2$ group is almost unaf-
fected. The group R2 suitably has at least 1 and prefer-
30   ably 2 CH$_2$ groups in a row closest to the group X2. In
longer chains of CH$_2$ groups, there is an increasing risk
of breakage. Thus, the number of CH$_2$ groups in a row
should not exceed 5.
          R2 suitably has at least one perfluorinated carbon
35   atom. Preferably this carbon atom is the end group of the
R2 group, that is a CF$_3$ group. More perfluorinated carbon
atoms result in better antisticking functionality. Very

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long carbon chains increase the risk of a break on the
chain and make the antisticking layer less stable, as
the carbon chains can change their angle to the surface.
Thus, R2 suitably has 1-12 perfluorinated carbon atoms,
5   preferably 2-8 perfluorinated carbon atoms and most pref-
erably 3-6 perfluorinated carbon atoms. The group R2 can
also be provided with shorter branches, suitably of a
length of 1-6 carbon atoms, more preferably 1-3 carbon
atoms, for instance with a view to increasing the anti-
10   sticking functionality or to enhancing the bond by
attaching to two groups X1.

$$X2-CH_2 \diagdown$$
$$\diagup CH-CF_2-CF_2-CF_3 \qquad \text{[branched group R2 with}$$
15     $$X2-CH_2 \diagup \qquad\qquad\qquad\qquad\qquad \text{stronger attachment]}$$

$$\diagup CF_3$$
$$X2-CH_2-CH_2-CF \qquad\qquad \text{[branched group R2 with}$$
$$\diagdown CF_3 \qquad\qquad \text{more CF}_3 \text{ groups]}$$
20

The last-mentioned variant, which is branched at the
end of the group R2 that is situated furthest away from
the group X2, has a larger "head". The nanostructured
pattern on the surface of the stamp is like a landscape
25   with crests and valleys. It may sometimes be difficult to
provide a sufficiently high density of the antisticking
functionality at the crests. An R2 group which is
branched and has two or more CF₃ groups at the end that
is not intended to bind to the first reagent fills out
30   the space better, thereby improving the antisticking
functionality at the crests, sharp corners and other
structures on the surface of the stamp.
It is suitable to select a second reagent, which
fulfils the criteria described above and which is avail-
35   able on the market. Examples of preferred second reagents
are thus 1H, 1H, 2H, 2H-perfluorooctanethiol:

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$SH-(CH_2)_2-(CF_2)_5-CF_3$
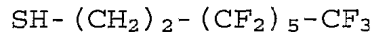
and fluorinated organic acid chlorides, such as 2H, 2H, 3H, 3H-perfluorohexaneacidchloride:

$Cl-(C=O)-(CH_2)_2-(CF_2)_2-CF_3$

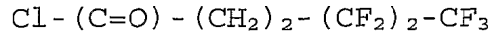According to a less preferred embodiment of the invention, one single reagent is used. This single reagent is bound in a reaction to the surface of the stamp. The reason why this embodiment is less preferred is that there are few commercially available compounds which, in one and the same compound, comprise suitable functional groups which can bind to the surface of the stamp, groups which have antisticking properties and in addition Q groups, which comprise a weaker bond. The single reagent used in this less preferred embodiment suitably has properties involving the above groups and being similar to the properties described above con-cerning the first and second reagents, with the exception that the above groups X1 and X2 are replaced by a group Q. Thus, this single reagent can, for instance, have the formula $(BO)_{3-n}R'_nSiR1QR2$, where the respective groups suitably have the properties and limitations described above. An example of a suitable single reagent in this less preferred embodiment is:

$$EtO-\overset{\displaystyle EtO}{\underset{\displaystyle EtO}{Si}}-CH_2-CH_2-CH_2-S-S-(CH_2)_2-(CF_2)_5-CF_3$$
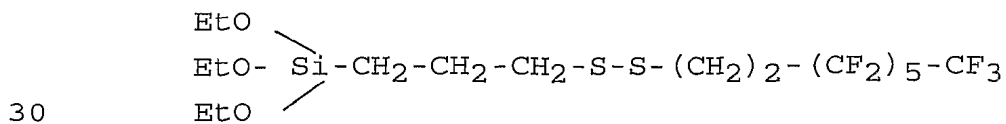
In a preferred method of manufacturing a stamp ac-cording to the invention, the nanostructured pattern is first formed on the surface of the stamp. This patterning can be effected, for instance, by etching or in some other prior-art manner. The surface which, for instance, can be a silicon surface, is subsequently cleaned by
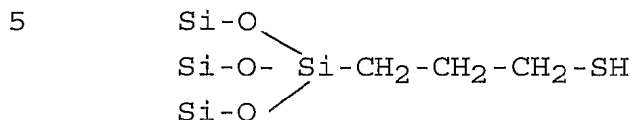
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means of, for instance, 1-4 organic solvents, such as trichloroethylene, ethanol, acetone and isopropanol, in succession. The last solvent is suitably isopropanol, which is particularly suitable to ensure that the surface

5   is free from water. In some cases, it is necessary to etch away the oxide layer of the surface, for instance, with fluoro-hydrogen acid, HF, (10-40% solution) to provide a homogeneous surface layer. The stamp is then treated with the first reagent. The first treatment can

10   be performed in either liquid phase or in gaseous phase.

In a first treatment in liquid phase, the stamp is placed for about 1-5 h in a vessel containing about 0.1-1% of the first reagent in an organic solvent, suitably an alkane, at room temperature. The stamp is then washed,

15   suitably by means of a series of 1-4 organic solvents similar to those mentioned above to remove the compounds which have not been covalently bound to the surface.

In a first treatment in gaseous phase, the stamp is placed in an oven with nitrogen gas atmosphere at a tem-

20   perature of about 50-250°C, suitably about 150-220°C, and at a pressure at which the first reagent is in gaseous phase, usually a pressure of about 0.5-20 kPa, suitably about 1-3 kPa. The exact combination of temperature and pressure is selected in such a manner that the current

25   first reagent is certain to be in gaseous phase. The first reagent is subsequently injected into the oven, vaporised and allowed to react with the stamp for about 0.5-10 h. Then the stamp is removed from the oven and allowed to cool, whereupon it is washed with a series of

30   organic solvents as described above.

The gaseous phase reaction is much more complicated to perform than the comparatively easy liquid phase reaction. Nevertheless, the gaseous phase reaction often yields a much more homogeneous monolayer on the surface

35   of the stamp and is thus preferable in many cases.

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Thus, in a silicon stamp and using the preferred
first reagents mentioned above, the following results can
be obtained after the first treatment:

5       $Si-O$
        $Si-O-\ Si-CH_2-CH_2-CH_2-SH$
        $Si-O$

or

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        $Si-O$
        $Si-O-\ Si-CH_2-CH_2-CH_2-NH_2$
        $Si-O$

15   Depending on the original structure of the surface,
the actual structure of the bond between the silicon
surface and the silane group as well as the residual
product, that is ethane or ethanol in the example above,
can be somewhat affected. It is assumed, although not
20 demonstrated, that the outermost layer of the surface can
have, for instance, the composition Si, SiH, SiOH or SiO
depending on how the surface has been treated. The bond
between the silicon surface and the silane group is
assumed to have the structure $(Si)_3Si$ or $(Si-O)_3Si$, but
25 the exact structure is not completely clear. The above
formulas are thus intended to designate a silane group
which is bound to a silicon surface, irrespective of the
exact structure of the actual bond.
        After that, the washed stamp is treated with the
30 second reagent. This second treatment can be effected
both in liquid phase and in gaseous phase.
        In a second treatment in liquid phase, the stamp is
placed in a vessel containing a suitable solvent, for in-
stance an alkane, with about 1-10% of the second reagent
35 at room temperature. The reaction is allowed to continue
for about 6-24 h, whereupon the stamp is taken out and
cleaned by dipping into one or more baths with a suit-

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able, organic solvent, for instance alkane as above. The
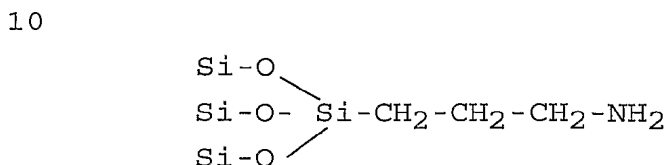stamp is then dried and ready for use in nanoimprinting.

In a second treatment in gaseous phase, the stamp is
placed in an oven with nitrogen gas atmosphere at a tem-
5   perature of about 50-200°C, preferably about 70-120°C.
The oven is evacuated to a low pressure, suitably about
1-20 kPa, more preferably about 5-10 kPa. The exact com-
bination of temperature and pressure is selected in such
a manner that the current second reagent is certain to be
10   in gaseous phase. The second reagent is injected into the
oven, vaporised and allowed to react for about 1-10 h
with the monolayer on the surface of the stamp. The stamp
is removed from the oven, allowed to cool, then cleaned
in the above-described manner and is subsequently ready
15   for use in nanoimprinting.

In the second treatment, the surface of the stamp is
already from the beginning covered with a monomolecular
layer. Consequently, a reaction in gaseous phase is usu-
ally not advantageous to the homogeneity of the layer.
20   The reaction in liquid phase is much more easy to perform
and normally preferable in the second treatment. However,
in case of very small nanostructures a reaction in gase-
ous phase is sometimes necessary to obtain a sufficiently
even layer after the reaction.

25   The groups X1 of the first reagent can sometimes be
bound to each other. One example is groups X1 in the form
of -SH groups which can form sulphur bridges, S-S, both
within one and the same molecule and between several
molecules. Therefore, the second reagent should be added
30   in large excess, since such an excess tends to break any
internal bonds between the groups X1 of the first re-
agent.

Thus, in a reaction between the above-described
product after the first treatment and the above-described
35   preferred second reagents, the following results can be
obtained after the second treatment when the groups X1

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and X2 have reacted and formed a group Q in the form of S-S and NH-C=O, respectively:

$$Si-O \diagdown$$
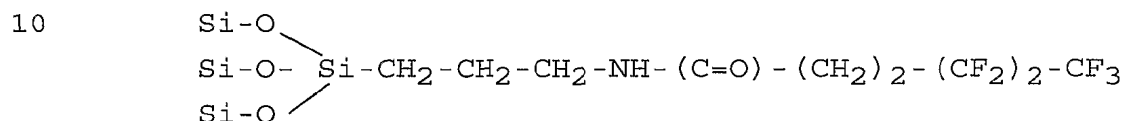5 $$Si-O- \quad Si-CH_2-CH_2-CH_2-S-S-(CH_2)_2-(CF_2)_5-CF_3$$
         $$Si-O \diagup$$

and

10       $$Si-O \diagdown$$
         $$Si-O- \quad Si-CH_2-CH_2-CH_2-NH-(C=O)-(CH_2)_2-(CF_2)_2-CF_3$$
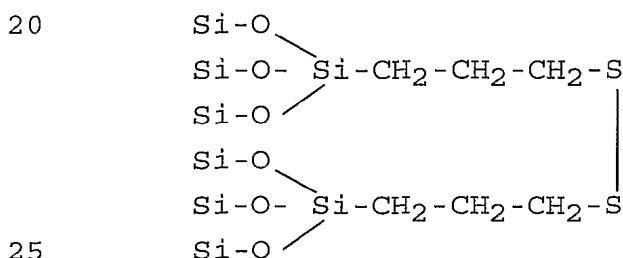 $$Si-O \diagup$$
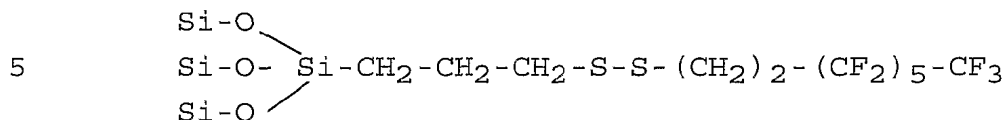
According to a less preferred embodiment, an anti-
15   sticking layer is formed by attaching directly a ready-
made molecular chain to the surface of the stamp, for
instance a molecular chain comprising a group which can
bind to the surface of the stamp, a Q group and at least
one fluorine-containing group. However, such a ready-made
20   molecular chain, which can for instance be in the form of
the above-described single reagent, is usually expensive
and difficult to obtain, which makes the above-described
preferred method comprising a first and a second treat-
ment in succession usually preferable to a direct attach-
25   ment in one step of a ready-made molecular chain. Attach-
ment of a ready-made molecular chain, in one single step
according to the last-mentioned, less preferred embodi-
ment, is performed substantially in the same manner and
under the same conditions as described above in connec-
30   tion with the first treatment.
        A ready-made group Q can also be included in the
first or the second reagent already from the beginning.
In such a case, the group Q is thus not formed of X1 and
X2.
35   When a stamp has been used for many nanoimprinting
operations, its antisticking layer may be damaged. Such
damage can arise when parts of the monomolecular layer

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get stuck to the polymer layer during embossing or the
layer can be damaged when the stamp is released from the
polymer layer after embossing or when the stamp is being
cleaned. It is normally very expensive to discard such a
5   damaged stamp and manufacture a new one.

According to a preferred embodiment of the inven-
tion, the group Q is selected so that a bond in the group
Q is somewhat weaker than the other bonds in the molecu-
lar chain as well as the covalent bond which attaches the
10 molecular chain to the surface of the stamp. The weaker
bond in the group Q will thus break first when the mo-
lecular chain is exposed to strain, for instance, tensile
or bending stress. A damaged antisticking layer will then
be deprived of its antisticking functionality but nor-
15 mally have an intact monomolecular layer comprising short
molecular chains with a well defined end group Q1 which
has formed when the group Q was split. Such a damaged
layer can have the following structure:

20      $Si-O$
        $Si-O- \ Si-CH_2-CH_2-CH_2-S$
        $Si-O /$
        $Si-O$
        $Si-O- \ Si-CH_2-CH_2-CH_2-S$
25      $Si-O /$

The end group Q1 shown above in the form of an in-
ternal sulphur bridge can instead be separate groups Q1
bound to the respective CH_2 groups in the form of -SH
30 groups depending on the conditions prevailing at the oc-
currence of the damage and how the stamp has been treated
since then. The damaged antisticking layer can easily be
repaired, thereby recovering its original antisticking
functionality in the following way. First, the stamp is
35 washed with some suitable organic solvent, for instance
an alkane. The stamp is then placed in a vessel which
contains a suitable solvent, for instance an alkane, with

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about 1-10% of a repairing reagent at room temperature. The reaction is allowed to proceed for about 6-24 h, whereupon the stamp is taken up and cleaned by dipping into one or more baths with a suitable, organic solvent,

5   for instance the above alkane. The stamp, which after the repair treatment has an antisticking layer of substantially the same quality as when the stamp was new, is subsequently dried and is then ready to be used again in nanoimprinting.
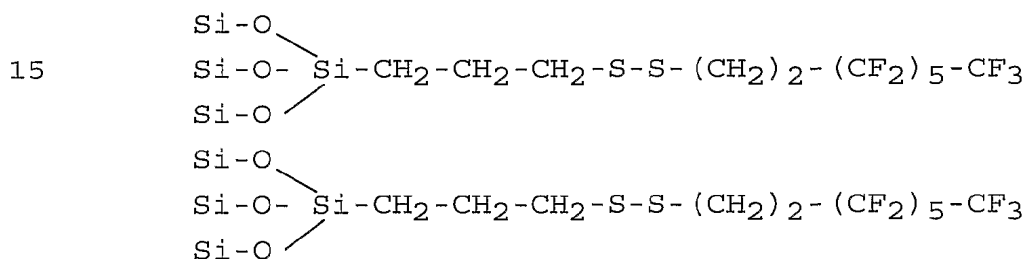
10   The repairing reagent will normally be the same compound as the second reagent which was used when the original antisticking layer was manufactured since such a repairing reagent normally yields the most even surface. It is, however, also possible to use a repairing reagent

15   that fulfils the above criteria for a second reagent, but that is not exactly identical to the second reagent which is used in the manufacture of the stamp. One example of the latter is that it can, under some conditions, be of interest during repair to attach a somewhat longer or more

20   branched molecular chain. The reason for this is that the wear on the antisticking layer is usually most important at the angles and similar structures where the surface coverage of the molecular chains is at its minimum. By binding a longer and/or more branched chain to these worn

25   positions when repairing, a thicker more resistant layer is obtained in exactly the positions of maximum wear.
        If the stamp has originally been treated with a ready-made molecular chain or a first or second reagent which contained a ready-made group Q, the repairing

30   reagent is suitably selected so as to resemble the "tail" which came off the molecular chain when the group Q was split.
        The repair treatment can also be carried out in gaseous phase. A treatment in gaseous phase is not as

35   easy as a liquid phase treatment, and since the quality of the repaired antisticking layer is often substantially the same, the liquid phase reaction is usually preferred.

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However, in case of very small nanostructures, that is
structures of a size of less than about 100 nm, the reac-
tion sometimes has to take place in gaseous phase in
order to obtain a sufficiently even layer after the re-
5   pair.

The repairing reagent should be added in large ex-
cess since this, for instance, makes the above-described
internal sulphur bridges break, whereby the monomolecular
layer on the surface of the stamp binds the repairing
10   reagent instead. After the repair, the surface of the
stamp will thus have, for instance, the following struc-
ture:

$$
\begin{array}{l}
\text{Si-O} \\
\text{Si-O-} \quad \text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-S-S-(CH}_2)_2\text{-(CF}_2)_5\text{-CF}_3 \\
\text{Si-O}
\end{array}
$$

$$
\begin{array}{l}
\text{Si-O} \\
\text{Si-O-} \quad \text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-S-S-(CH}_2)_2\text{-(CF}_2)_5\text{-CF}_3 \\
\text{Si-O}
\end{array}
$$

20

Therefore, one advantage of the present invention is
that two relatively simple and cheap compounds, in the
form of the first and the second reagent, can be used to
form a stable antisticking layer with satisfactory chemi-
25   cal and mechanical properties. By using a group Q, the
antisticking layer can be restored when damaged or worn.
In a particularly preferred embodiment, in which the bond
Q is weaker than the other bonds in the molecular chain,
a well-defined fracture surface is obtained in case of
30   damage, which surface does not have a detrimental effect
on the ordered monomolecular structure. Then the
antisticking layer can easily be repaired by the addition
of a repairing reagent.

The expression "weaker" is used above for a bond,
35   which unites a molecular chain and is included in the
group Q, in the sense that said bond is weaker than the
other bonds in the molecular chain as well as the bond

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that attaches the molecular chain to the surface of the
stamp under the conditions (such as temperature, pres-
sure, etc) prevailing in the nanoimprinting process.
The expression "weaker" in connection with said bond is,

5   however, to be interpreted in a wider sense. It is, for
instance, possible to select a group Q which has a bond
that is weaker under specific conditions. For instance,
a stamp with a worn antisticking layer can, in connection
with a repairing process, first be subject to conditions

10   such that substantially all the groups Q are split,
whereby a monomolecular layer is obtained in which each
molecular chain has a group Q1 as end group. This layer
can then be repaired by the addition of a repairing
reagent according to that stated above. One advantage

15   of exposing the stamp to conditions under which all the
groups Q are split is that also molecular chains, which
have been damaged in the embossing without the group Q
being split, for instance molecular chains in which only
the actual fluorine-containing group has been damaged,

20   can be repaired. It will also be possible to repair
damage which has occurred close to the surface of the
stamp, since it will be easier for new molecules, which
are intended to bind directly to the surface of the
stamp, to reach the surface when the groups Q have been

25   split and a "tail" has been removed from each molecular
chain.
   Examples of Q groups which are weaker under some
conditions are esters and thioesters. In the former case,
the surface of the stamp can first be provided with a

30   first reagent in the form of an alcohol, for instance:

         EtO
   EtO   — $Si-CH_2-CH_2-CH_2-OH$
         EtO
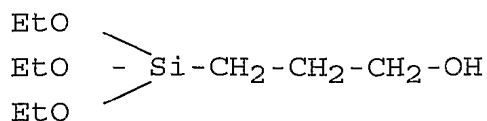
35

The first reagent is attached to the surface of the stamp,
whereupon the stamp is treated with a second reagent in

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the form of a carboxylic acid, which for instance results
in the following compound on the surface of the stamp by
esterification:

5   Si-O
       Si-O- Si-CH$_2$-CH$_2$-CH$_2$-O-(C=O)-(CH$_2$)$_2$-(CF$_2$)$_2$-CF$_3$
       Si-O
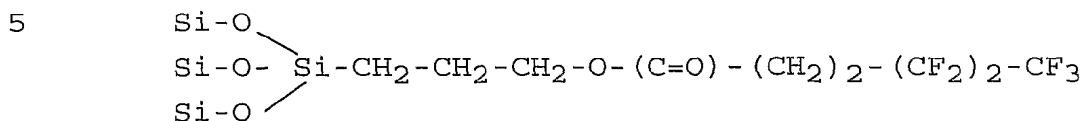
It is also possible to use a first reagent with an -SH
10   group, in which case a thioester is formed, for instance:

       Si-O
       Si-O- Si-CH$_2$-CH$_2$-CH$_2$-S-(C=O)-(CH$_2$)$_2$-(CF$_2$)$_2$-CF$_3$
       Si-O
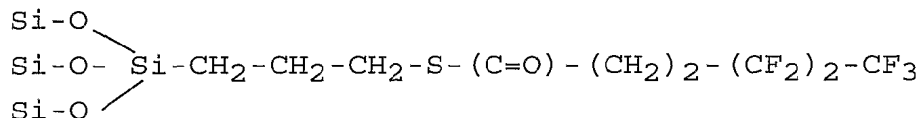
15

Naturally, it is also possible to first attach a first
reagent with a carboxylic acid group to the surface of
the stamp and then allow this carboxylic acid group to
react with a second reagent in the form of a thiol or an
20   alcohol. As the carboxyl acid group, under some condi-
tions, can react with the surface of the stamp, this is
less preferable.
       The above ester bonds and thioester bonds are very
strong bonds, which can be broken by dipping the stamp
25   into a beaker which contains a liquid, such as a hydro-
chloric acid solution, with a low pH, for instance pH 0-
2, which results in an acid ester hydrolysis, or a
liquid, such as a sodium hydroxide solution, with a high
pH, for instance pH 10-13, which results in an alkaline
30   ester hydrolysis. In both cases, a group Q1 forms on the
part of the respective molecular chains that is left on
the surface of the stamp, which group Q1, after washing
of the stamp, can react with a repairing reagent to re-
store the antisticking layer of the stamp.
35   Another example of the conditions under which a bond
in the Q group is weaker is when affected by an enzyme.
In this case, the stamp is dipped into a beaker which

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contains an aqueous solution with a suitable enzyme. The enzyme breaks bonds in Q groups and forms Q1 groups on the part of the respective molecular chains that is left on the surface of the stamp. After the enzyme treatment,

5   the stamp is washed and can be repaired as described above. Examples of bonds that are weaker under the influence of a suitable enzyme are peptide bonds, which can be split by peptidases, for instance endopeptidases, such as pepsin, trypsin, papain, as well as ester bonds

10   and thioester bonds, which can be split by peptidases, for instance carboxy peptidases, such as carboxy peptidase A.

It is also conceivable to etch away the entire molecule layer, for instance, by etching with hydro-

15   fluoric acid, HF, which attacks the surface layer of the stamp, such as silicon dioxide groups in case of a silicon surface, and subsequently attach a completely new molecule layer to the stamp according to one of the above-mentioned methods.

20   Example 1

A stamp made of silicon was etched to form a nano-structured pattern. The stamp was washed with, in succession, trichloroethylene, ethanol and isopropanol. The stamp was subsequently dipped into a beaker with hexane

25   at room temperature with 0.2% mercaptopropyltriethoxy-silane, which corresponded to an excess amount of mer-captopropyltriethoxysilane, and was allowed to react for 4 h. The stamp was then removed from the beaker and cleaned with, in succession, trichloroethylene, ethanol

30   and isopropanol. The stamp was dried and subsequently placed in a beaker, which contained hexane at room temperature with 2% 1H, 1H, 2H, 2H-perfluorooctanethiol. After 16 h, the stamp was removed from the vessel, washed with hexane in three successive baths and then dried. The

35   stamp was tested in a nanoimprint lithography process and was found to resist 50 embossings without any particular signs of wear being detected.

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Example 2

A stamp made of silicon was patterned and washed in
the manner described in Example 1. The stamp was subse-
5   quently placed in an oven, which had a temperature of
200°C and was evacuated to a pressure of 1 kPa. Mercapto-
propyltriethoxysilane was injected in large excess into
the oven and vaporised. The stamp was allowed to react
with the mercaptopropyltriethoxysilane for 3 h and was
10   then removed from the oven and allowed to cool. The stamp
was cleaned and treated with 1H, 1H, 2H, 2H-perfluoro-
octanethiol in liquid phase in the manner described in
Example 1. The stamp was tested in a nanoimprint litho-
graphy process and was found to resist 50 embossings
15   without any particular signs of wear being detected.

Example 3

The experiment in Example 2 was repeated with mate-
rials and reagents according to Table 1:

20   Table 1. Combinations of materials and compounds used in
Example 3.

Surface of the stamp	First reagent	Second reagent
Si	$(MeO)_3Si(CH_2)_3NH_2$	$Cl(C=O)(CH_2)_2C(CF_3)_3$
Si	$Cl_3Si(CH_2)_3SH$	$SH(CH_2)_2(CF_2)_7CF_3$
Si	$(EtO)_3Si(CH_2)_3OH$	$HO(C=O)(CH_2)_2(CF_2)_2CF_3$
Al	$(MeO)_3Si(CH_2)_3SH$	$SH(CH_2)_2(CF_2)_5CF_3$
Al	$Cl_3Si(CH_2)_3SH$	$SH(CH_2)_2(CF_2)_2CF_3$
Ni*	$(EtO)_3Si(CH_2)_3SH$	$SH(CH_2)_2(CF_2)_5CF_3$
Ti	$(EtO)_3Si(CH_2)_3SH$	$SH(CH_2)_2(CF_2)_5CF_3$

*The surface of Ni was first treated with an oxygen
plasma to oxidise the surface.

25   The finished stamps were tested in a nanoimprint
lithography process and all of them were found to resist
50 embossings without any particular signs of wear being
detected.

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Example 4

A stamp manufactured according to Example 2, after several hundred embossings, started to show signs of

5 sticking to the polymer layer when the stamp was to be removed after embossing. The sticking was detected by examining the surface of the stamp in an optical microscope, which showed that residues of the polymer layer were stuck to the surface of the stamp. The stamp was

10 cleaned by being dipped into three successive baths with hexane. The stamp was then placed in a beaker which contained hexane at room temperature with 2% of 1H, 1H, 2H, 2H-perfluorooctanethiol, which was present in large excess. After 16 h, the stamp was removed from the ves-

15 sel, cleaned with hexane in three successive baths and then dried. The repaired stamp was tested in a nanoimprint lithography process and was found to resist 50 embossings without any particular signs of wear being detected. The antisticking functionality of the repaired

20 stamp was, as far as could be judged, equal to that of a new stamp.

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CLAIMS

1. A stamp for use in transferring a pattern in nanoscale, which stamp has a monomolecular antisticking layer, c h a r a c t e r i s e d in that said anti-sticking layer comprises molecular chains, which are covalently bound to the surface of the stamp and which each comprise at least one fluorine-containing group, each molecular chain containing a group Q, which comprises a bond which is weaker than the other bonds in the molecular chain as well as the covalent bond that binds the molecular chain to the surface of the stamp, splitting of said bond in the group Q creating a group Q1, which is attached to the part of the molecular chain being left on the surface of the stamp and which is capable of reacting with a fluorine-containing compound to restore the antisticking layer.

2. A stamp as claimed in claim 1, in which the anti-sticking layer comprises a silane group.

3. A stamp as claimed in claim 2, in which the sur-face of the stamp is made of a material M, which is se-lected from silicon, aluminium, nickel, chromium and titanium or oxides thereof, the silane group of the anti-sticking layer being bound to the surface by means of at least one group B1, which is selected from M- and M-O-.

4. A stamp as claimed in claim 3, in which the anti-sticking layer has a first part, which has the general formula $(B1)_{3-n}R'_nSiR1X1$, where n is 0, 1 or 2, R' is an aliphatic, saturated carbon compound, Si is the silane group, R1 is a carbon chain and where X1 is a first coupling group, and a second part, which has the general formula X2R2, where X2 is a second coupling group which is bound to X1 and which together with X1 forms the group Q and where R2 is a fluorine-containing hydrocarbon com-pound.

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5. A stamp as claimed in claim 4, in which R1 is a carbon chain which has a length from the silane group to X1 of 2-10 carbon atoms and preferably is saturated and unsubstituted.

6. A stamp as claimed in claim 4, in which R2 is a carbon chain which has a length from the end group to X2 of 2-10 carbon atoms and preferably comprises at least one perfluorinated carbon atom and is saturated.

7. A stamp as claimed in claim 6, in which R2 is branched at the free end, each branch comprising at least one perfluorinated carbon atom.

8. A stamp as claimed in claim 4, in which n is 0.

9. A stamp as claimed in any one of the preceding claims, in which the group Q is a sulphur bridge.

10. A method of manufacturing a stamp for use in transferring a pattern in nanoscale, which stamp has a monomolecular antisticking layer, c h a r a c t e r - i s e d in that the surface of the stamp is provided with molecular chains, which are covalently bound to the surface of the stamp and which each comprise at least one fluorine-containing group and a group Q, which comprises a bond which is weaker than the other bonds in the mo- lecular chain as well as the covalent bond that binds the molecular chain to the surface of the stamp, splitting of said bond in the group Q creating a group Q1, which is attached to the part of the molecular chain being left on the surface of the stamp and which is capable of reacting with a fluorine-containing compound to restore the antisticking layer.

11. A method as claimed in claim 10, in which the surface of the stamp is treated by

being reacted with a first reagent, which has a first functional group, which is hydrolysable, and a second functional group,

thus binding the first functional group of the first reagent to the surface of the stamp,

subsequently treating the surface of the stamp with a second reagent, which has a first end, which is capable of reacting with the second functional group of the first reagent, and a second end, which comprises at least one fluorine-containing group, and

binding the first end of the second reagent to the second functional group of the first reagent, thereby forming the group Q.

12. A method as claimed in claim 11, in which the first reagent is converted into gaseous phase before it is reacted with the surface of the stamp.

13. A method as claimed in claim 11 or 12, in which the treatment with the second reagent is carried out in liquid phase.

14. A method of repairing a damaged monomolecular antisticking layer on a stamp as claimed in claim 1, c h a r a c t e r i s e d   i n

that the stamp is treated with a repairing reagent, which has a coupling end, which is capable of reacting with the group Q1, and a fluorine-containing group located at the other end of the repairing reagent,

that the coupling end of the repairing reagent is bound to the group Q1 which is attached to the surface of the stamp, the group Q being formed anew.

15. A method as claimed in claim 14, in which the stamp is first treated for splitting substantially all groups Q.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 02/01334

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: G03F 7/00, B41M 1/06, B82B 1/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, PAJ, WPI DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6027595 A (SULESKI), 22 February 2000 (22.02.00), column 2, line 27 - line 29 --	1-15
A	WO 0054107 A1 (BOARD OF REGENTS, THE UNIVERSITY OF TEXAS SYSTEM), 14 Sept 2000 (14.09.00), page 6, line 6 - line 14 --	1-15
A	WO 0000868 A1 (REGENTS OF THE UNIVERSITY OF MINNESOTA), 6 January 2000 (06.01.00), page 9 -- ---------	1-15

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 Sept 2002	1 1 -10- 2002
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Authorized officer Bengt Christensson/ELY Telephone No. + 46 8 782 25 00

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WO	0054107	A1	14/09/00	EP 1228401 A US 6334960 B US 2001040145 A		07/08/02 01/01/02 15/11/01
WO	0000868	A1	06/01/00	AU 1021900 A CN 1309784 T EP 1127107 A US 6309580 B WO 0026347 A		22/05/00 22/08/01 29/08/01 30/10/01 11/05/00